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PREPARATION OF DIHEPTYLDITHIOPHOSPHORIC ACID AND IT'S USE AS AN EXTRACTANT IN LIQUID-LIQUID EXTRACTION

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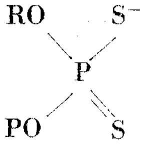
ABSTRACT

Diheptyldithiophosphoric acid was prepared from the reaction of phosphorus pentasulfide with heptanol and purified with lime slurry. The solvent extraction of Ni(II), Cu(II), Co(II), and Zn(II) metal ions as diheptyldithiophosphates from aqueous solutions into an organic phase, and the possibility of their separation from one another have been investigated.

INTRODUCTION

Organophosphorus compounds, both neutral and acid, provide a versatile range of solvent extraction reagents. Using of alkyl phosphates such as, tributylphosphate (TBP), di–(2–ethyl hexyl) phosphoric acid (HDEHP), dibutylphosphate (DBP) for extraction of metal ions from aqueous solutions is well known (Miyake, 1989; Korkisch, 1969; Fidelis, 1980; Madigan, 1960). Organophosphorus compounds have been extensively investigated, but less is known about their analogues where one or more oxygen atoms have been replaced by sulfur atoms. The presence of sulfur atoms is attractive because of the chemical properties they are expected to give to the molecules, properties which can be predicted by Pearson's "Hard and Soft Acids and Bases (HSAB)" Principle (Huheey, 1978). Many authors have prepared and tested various organothiophosphorus extractants in order to find selective extractants for soft (Pd (II), Pt(II), Ag(I), Cd(II), Hg(II) e.t.c.) and borderline (Co(II), Cu(II), Ni(II), Zn(II), e.t.c.) metal cations (Cote, 1989; Handley, 1962; Levin, 1973; Zucal, 1963; Wingefors, 1980; Toropova, 1978; Mazitova, 1980; Ganguli, 1987). In recent years the metal chelate compounds of dialkyldithiophosphoric acids attracted considerable interest (Cote, 1989; Marcu, 1979). Almost without exception, the anion of these acids (II) acts as a bidentate ligand, to form inorganic four–membered chelate rings (II). Most of these metal chelates are soluble in organic solvents and insoluble in water, which makes them useful in the solvent extraction of many metal ions.



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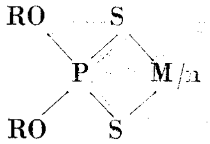

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It was known that dialkyldithiophosphoric acids are quite strong with pKa around zero and their complexes with the heavy soft metals are extractable even in strongly acidic solutions (Cote, 1989; Handley, 1962; Wingefors, 1980).

Dialkyldithiophosphoric acids containing different alkyl groups such as diethyl–, dipropyl–, dibutyl–, di–(2–ethyl hexyl)–, e.t.c. were synthesised and have been throughly investigated as selective extraction reagents for hydrometallurgical purposes (Handley, 1962; Levin, 1973; Zucal, 1963; Mazitova, 1980; Curtui, 1981). No extensive studies have been made on higher homologues of dialkyldithiophosphoric acids because of some difficulties in their preparation and purification.

In this work we have prepared and purified diheptyldithiophosphoric acid and used it as an extraction reagent for Ni(II), Cu(II), Co(II) and Zn(II) metal ions from acidic aqueous solutions.

EXPERIMENTAL

Preparation and Purification of Diheptyldithiophosphoric Acid.

Diheptyldithiophosphoric acid (HDHpDTP) was prepared from the reaction of phosphorus pentasulfide (Fluka–79600) with heptanol (Fluka 51790).

$$4\ C_7H_{15}OH + P_2S_5 \longrightarrow 2\ (C_7H_{15}O)_2P(S)\,SH + H_2S$$

In order to make a sufficiently pure compound, the method described in the literature had to be somewhat modified (Levin, 1973; Wingefors, 1980; Mazitova, 1980). 44.4 g of phosphorus pentasulfide was added to 92.8 g of anhydrous heptyl alcohol with constant stirring. The reaction was performed under nitrogen atmosphere at 70°C for 6 h. The mixture was cooled and the unreacted solid part was filtered. Titration of a 10 % solution of the liquid part (Technical extractant) in ethyl alcohol with 0.1007 N solution of sodium hydroxide showed that the product contained about 89 % HDHpDTP. The rest could be unreacted heptanol and other compounds containing P, S, or 0 (Wingefors, 1980).

The acid was then converted to calcium salt by neutralization with lime slurry (calcium hydroxide) at room temperature. The salt was separated from the aqueous phase, washed with hexane, and acidified with 3M H_2SO_4. Calcium was precipitated as $CaSO_4$ and the free acid (light yellow-green) floating on top of aqueous pahase was separated (Table-1). When NaOH solution used instead of lime slurry, some problems were observeb. Attempts to purify HDHpDTP (89 %) by vacuum distillation (at 4 mm Hg, 120°C) gave unfavourable results (Table-2).

Table 1. Some properties of the raw and purified diheptyldithiophosphoric acid.

Element Analysis	Found		Calculated
	Raw Product	Purified Product	
C %	52.06	51.67	51.49
H %	10.40	9.78	9.57
P %	8.94	9.21	9.50
Refractive index	1.486 (3)	1.474 (2)	——
Density (g / ml)	0.9931	0.9699	——
Percent of the acid (W / W)	89	97	——

Table 2. The purification of HDHpDTP (89 %) by vacuum distillation (at 4 mmHg, 120'C).

Fractions	HDHpDTP (%)	Ref. Index
Raw material	89	1.486 (3)
Over flow	49.1	1.470 (2)
Distilled	15.4	1.457 (2)
Residue	35.3	1.518 (8)

Characterization of HDHpDTP

1) UV-Visible Spectra: Spectra of the HDHpDTP in carbon tetrachloride was taken with Schimadzu UV-160 automatic recording spectrophotometer (Figure-1).

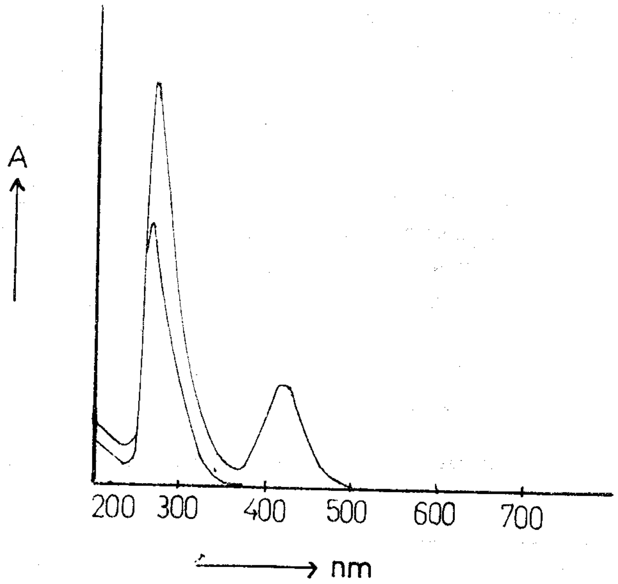

Fig. 1. UV–Visible spectra of HDHpDTP and its Cu(II) complex.

2) **Infrared Spectra:** The infrared spectra of HDHpDTP and its complexes were obtained in carbon tetrachloride by IR Rank–Hilger Spectrophotometer (Figure–2).

3) **Analytical Procedures:** Carbon and hydrogen analyses were carried out at the Laboratories of the Scientific and Technical Research Council of Turkey. Phosphorus was determined spectrometrically at 430 nm by Spectronic–20D (Bosch and Lomb) Visible Spectrophotometer (Table–1).

4) **Potentiometric Titration:** A solution of the acid in ethyl alcohol is titrated with NaOH solution and results are show in Figure–3.

All other reagents were used as provided from commercial sources and were of analytical grade purity.

0.002 M Mixed stock solution of Ni(II), Cu(II), Co(II) and Zn(II) was prepared by dissolving appropriate amounts of the investigated element salts in distilled water. The aqueous phases (0.001 M) were obtained from this stock solution. Various pH values were attained

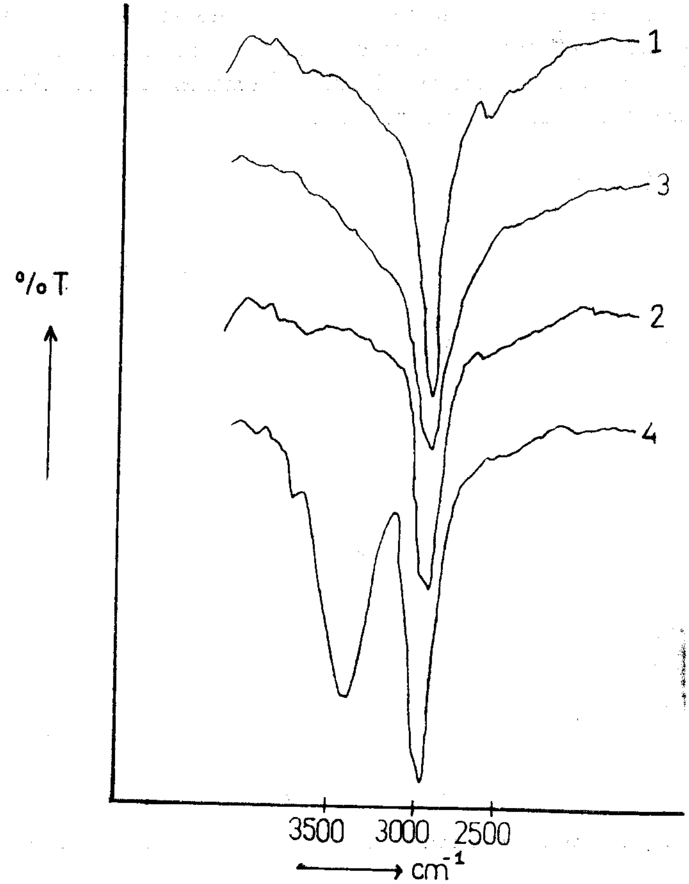

Fig. 2. IR spectra of; 1) Purified HDHpDTP, 2) Technical HDHpDTP, 3) Cu (II) complex of HDHpDTP, 4) n-heptanol.

by using sulfuric acid or sodium hydroxide. The pH of solutions were determined with an Orion Research Model 701 pH-meter.

Carbon tetrachloride, ethyl acetate, gasoline, kerosene, benzene, petroleum ether, and n-hexane were used as solvent.

Extractions were carried out by stirring equal volumes (25 ml) of the organic and aqueous phases for 5 minutes at room temperature in a separatory funnel of conventional design. Preliminary experiments indicated that the distribution equilibrium was usually achieved less than 5 minutes. After separation of the phases an aliquot of aqueous part was analyzed for the particular metal concentrations by atomic absorption spectrophotometer (Varian–Techtron Model 1200). The results are shown in Table–3 to Table 6.

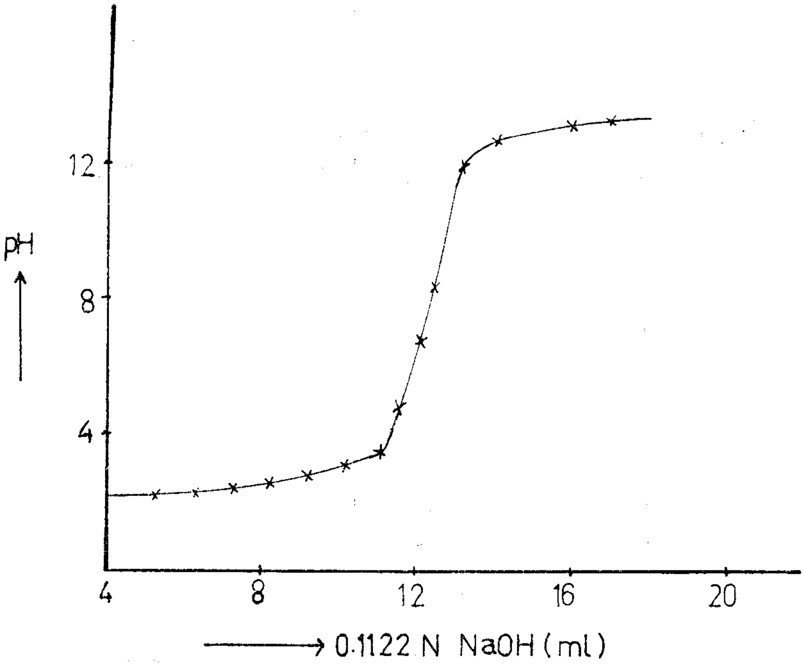

Fig. 3. Potentiometric titration of HDHpDTP with 0.1122 N NaOH

Table 3. Effect of organic solvent on the extraction (initial pH = 1.95; 2.5 % HDHpDTP)

Solvent	pH Equilibrium	Extraction (%)			
		Cu (II)	Co (II)	Ni (II)	Zn (II)
Gasoline	1.69	79	100	100	100
Kerosene	1.69	76	100	100	100
Ethylacetate	1.68	85	98	100	99
Petroleum ether	1.69	77	100	100	100
n–Hexane	1.61	80	100	100	100
Benzene	1.67	89	97	98	98
Carbontetra chloride	1.21	96	100	96	99

Back–Extraction studies were carried out with sulfuric acid and hydrochloric acid solutions (Table–7).

Table 4. Influence of HDHpDTP concentration on the extraction (ini. pH = 1.02; kerosene as solvent).

HDHpDTP, %	pH Equilibrium	Extraction (%)			
		Cu (II)	Co (II)	Ni (II)	Zn (II)
5	0.70	72	100	100	100
2.5	0.95	87	72	100	88
1	0.95	100	15	88	60
0.5	0.95	100	3	50	28
0.25	0.96	100	0	18	2
0.1	0.96	100	0	0	0

Table 5. Effect of sulfuric acid concentrations on the extraction (5 % HDHpDTP in kerosene).

pH		Extraction (%)			
Initial	Equilibrium	Cu (II)	Co (II)	Ni (II)	Zn (II)
2 M	——	96	29	20	49
1 M	——	96	29	25	53
0.5 M	——	96	46	55	72
1.07	0.7	72	100	100	100
1.96	0.8	69	100	100	100
2.90	0.8	63	100	100	100
4.00	1.3	56	96	100	100
4.90	1.3	53	98	100	100

RESULTS AND DISCUSSIONS

Diheptyldithiophosphoric acid (HDHpDTP) was prepared by the reaction of n–heptanol with phosphorus pentasulfide. 122.34 gram product obtained and contained about 89 % HDHpDTP with a recovery of 83.2 %. This technical extractant was easily purified to

Table 6. Effect of sulfuric acid concentrations on the extraction (1 % HDHpDTP in kerosene).

pH		Extraction (%)			
Inital	Equilibrium	Cu (II)	Co (II)	Ni (II)	Zn (II)
2 M	—	100	9	10	—
1 M	—	100	9	18	8
0.5 M	—	100	—	37	10
1.00	1.00	100	11	95	54
1.97	1.87	98	98	100	100
2.95	2.08	98	100	100	100
3.98	2.24	96	100	100	100
5.20	2.28	94	100	100	100

Table 7. Reextraction of some elements from kerosene phase.

Acids	Reextraction (%)			
	Cu (II)	Co (II)	Ni (II)	Zn (II)
1 M H_2SO_4	0	10	90	98
3 M H_2SO_4	0	11	93	77
5 M H_2SO_4	0	13	85	56
7 M H_2SO_4	0	15	42	44
3 M HCl	0	0	88	87
5 M HCl	0	0	84	80
7 M HCl	0	0	78	54

97 % HDHpDTP by using lime slurry (Table–1). Some problems were observed during the purification of the acid with NaOH (Purity 95 %).

In order to obtain 98–99 % di–(2–ethyl hexyl) dithiophosphoric acid from the raw acid Levin and co–workers used NaOH, KOH and the purification was repeated 2–3 times.

It can be seen from Table–2 that, because of the decomposition of the acid, unfavorable results were obtained during the vacuum distillation of the acid.

The characteristic bands of P(S)SH group of UV–visible and IR spectra of the acid and its complexes are shown in Figure-1 and Figure-2.

The results are in agreement with the earlier studies on the other dialkyldithiophosphoric acids (Levin, 1973). The peak at 262 nm is related to P(S)SH group. The absorption band due to the stretching vibation of the S–H group (at ca. 2550 cm^{-1}) that characterize the acid have disappeared, when its M^{+2} complexes prepared (Figure–2).

The potentiometric titration of the acid with a solution of sodium hydroxide (Figure–3) showed that the acid is monobasic, and the titration curve is indistinguishable from that of a strong monobasic acid.

Preliminary experiments on the extraction indicated that there was no significant difference between the technical HDHpDTP (89 %) and the purified HDHpDTP (97 %). Therefore, when the acid is employed in hydrometallurgy, there is no need to purify it.

A systematic study was made on the extraction of Ni(II), Cu(II), Co(II), and Zn(II) elements, for which the results are presented in Table–3 to Table –6. All data are for one batch contact with an initial concentration of HDHpDTP in organic solvent.

The influence of various organic solvents (such as carbon tetrachloride, ethyl acetate, kerosene, benzene, petroleum ether, gasoline, and n–hexane) on the extraction of the metal ions were investigated and the results are shown in Table–3. It can be seen from the Table–3- that, the effect of different organic solvents on the extraction is negligible.

The effect of HDHpDTP concentrations in organic phase have greatest significance for use in extraction (Table–4, Table–5, and Table–6). Table–4 shows that, when 0.1 % of HDHpDTP / kerosene was used in the extraction, only Cu(II) was extracted quantitatively and Ni(II), Co(II), and Zn(II) were remained in the aqueous phase. Thus it could be possible to separate Cu(II) from the others.

It can be seen from the Table–4, Table–5, and Table–6 that, the extraction efficiencies of Cu(II) into organic phase decrease with increasing HDHpDTP concentrations.

For investigation of the effect of pH in aqueous solutions, H_2SO_4 concentrations were varied from 2M to neutral values. pH of the aqueous solutions were determined before and after extractions. It can be seen from Table–5, and Table–6 that, Ni(II), Co(II), and Zn(II) were extracted quantitatively in the range $1 < pH < 5$ from aqueous solutions. Among the metal ions, Cu(II) was extracted completely at $pH < 1$ into organic media.

Results of back-extraction studies are shown in Table-7. It can be seen from Table-7 that, Ni(II), and Zn(II) were re-extracted easily by 1M of H_2SO_4 while Co(II) was remained in the organic phase. The back extraction of Cu(II) could not be achieved by using H_2SO_4 solutions up to 10M. Cu(II) remains quantitatively in the organic phase and this property can be used for analytical purposes.

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